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Irradiation detection of oilseed crops by electron spin resonance

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Abstract The ESR signal of black sesame, soybean, peanut irradiated with 0–9 kGy absorbed dose was determined and the characteristics and intensity were different. The relationship between signal intensity and absorbed doses was also investigated .The results showed that the ESR spectra of irradiated samples inhibited obvious variation compared to those un-irradiated. The dose-response curves of the samples exposed to gamma rays could be described well by binomial function. Besides, the ESR signal intensity was related to the species of samples. This study may be a method for detection of irradiated oilseed by ESR.

Key words Irradiation, Detection, Electron spin resonance (ESR)

1 Introduction

Oilseed crops are one of the most important agricultural products for international trade. Most oilseeds crops are consumed as roasted, extracted oil and steamed products. However almost 25% of this kind of agricultural products would mildew or suffer insect infestation before consume. Food irradiation, which was also known as cold pasteurization, was used to ensure food safety and sterility by eliminating, or minimizing pathogenic organisms. This processing of food involves in controlled application of energy from ionizing radiations such as gamma rays, X-rays, and electron beams for food preservation which can not only enhance the shelf lives of the food but also optimize the storage conditions[1–3]. The ionizing radiation is strong enough to produce free radicals from an atom[4]. Eliciting structural damages cause by those free radicals inhibited multiplication of the microbe that leads to physiological changes to result in the microorganism's inability to replicate[5]. Almost 40 countries, including India, have approved the use of irradiation for over 100 food items, but in some countries it is prohibited. In order to facilitate international trade, control of irradiated food can be supported by analytical methods which are suitable to detect directly in the product whether or not it has been treated with radiation using the food itself as a radiation marker[6,7].

Based on physical, chemical, biological, and microbiological changes in food products during irradiation process, there are various methods used for the detection of irradiated foods such as physical methods, chemical methods, biological methods, and DNA methods. Thereinto, physical methods include Electron spin resonance spectroscopy (ESR), Luminescence techniques, Thermo-luminescence (TL), Photoluminescence (PL), and Chemo-luminescence (CL)[8–10]. The ESR principle is based on the quantum theory and it detects the irradiation-produced long-lived paramagnetic active sites of the free radicals in the organic and inorganic complexes which has been accepted as a standard method (Committee Europe de Normalization) in the EU Community. ESR spectroscopy is charactered by rapidity, specific, easy to performing, and quantitative estimation[10,11]. it is used in the irradiation detect in a wide variety of foods, packaging materials, and so on.

This paper aims at detecting the minimum physical and chemical change in the irradiation

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process of the oilseed samples (black sesame, peanut, and soybean) by ESR. Detection of irradiated peanut and black sesame has been studied by many scientists using ESR technique respectively[12]. However, no papers have been reported about ESR study with oilseeds, and crops to discuss the similarities and distinction among them. The ESR investigation on irradiated oilseeds will be described in our work.

2 Materials and methods

Oilseed samples (black seamed, soybean and peanut) purchased from local farmers in Hangzhou China, were dried by the electric vacuum drying oven until water reaching (8±2)% then crushed with a high speed crusher. Samples were packed (10 g per pack) with low-density polyethylene ziplock bag and divided into two parts, one part for irradiation and another for control. Samples were irradiated at room temperature, by a ^{60}Co gamma source at the Institute of Nuclear Agriculture Science of Zhejiang University in Hangzhou (China) with a dose rate of 0.5 kGy/h and absorbed doses at 0.5, 1, 2, 3, 5, 7 and 9 kGy, respectively by setting five parallel samples (10 g per pack) for each irradiation dose. The absorbed dose was calibrated with standard silver dichromate (Fricke dosimeter). The uncertainty in radiation doses was nearly ±3%. The samples were protected from light during irradiation and stored at room temperature ((20± 2)°C) in the dark for further measurement.

ESR measurements of un-irradiated (control) and irradiated samples were performed at normal laboratory conditions (about 20±2ºC and 30±2% relative humidity) as soon as possible after the irradiation. The ESR spectra were conducted to Bruker A-300 (9-10GHz) spectrometer equipped with a cylindrical cavity. The quartz tubes with inner diameter of 5 mm were filled with nearly 30 mg of whole seed samples for each measurement. The tube was centered in the microwave cavity exactly in the same position. The spectrometer parameters were central field 336 mT, microwave power 0.5 mW, modulation frequency 100 kHz, modulation amplitude 0.4 mT, scan range 10 mT, and sweep time 49.925 s. The strong pitch (g=2.0028) was used as a standard sample for measuring g-factor. Each data point was the average of at least four independent measurements. The experimental error was estimated to be ±5%. In this work, the intensity of the ESR was measured as the peak-to-peak height of the signal.

3 Results and discussion

3.1 ESR spectra of un-irradiated (control) and irradiated oilseed samples

An ESR singlet was observed in ESR spectra of all irradiated and un-irradiated (control) oilseed samples. In the case of the irradiated samples, the intensity of singlet increased with the irradiation dose significantly. The ESR spectra of the un-irradiated and irradiated samples of oilseed crops are shown in Fig.1.

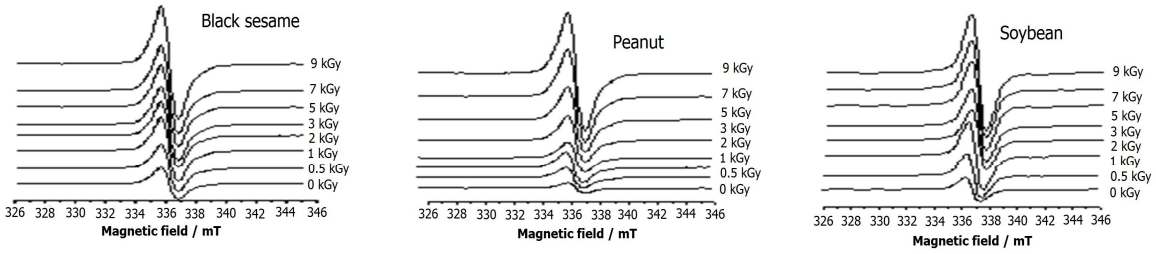

Fig.1 ESR spectra of soybean, peanut and black sesame after irradiation.

It has been found the un-irradiated samples also have an ESR signal which can be assigned to cellulose in the plant reported by Seiichi Saiki *et al.* 2011 meanwhile crushing and storing samples may produce ESR singlet. In the range of the irradiation dose, the ESR intensity has a positive correlation with the absorbed dose. Similar correlation were also obtained for another foodstuff[13]. It can easily distinguish the irradiated oilseeds (black sesame, peanut, and soybean) if absorbed dose is over 0.5 kGy.

3.2 Dose-response curve

As shown in Fig.2 the ESR singlet in the central field 336 mT increased with absorbed doses. The relationship between intensities of ESR and absorbed doses can be described with fitting function as listed in Table 1. Here Y represents ESR intensity which derived from peak-to-peak amplitude of the ESR singlet, X represents absorbing dose, R^2 represents correlation coefficient. T Jeongeun lee had report that hydrocarbons and 2-alkylcyclobutanones could form during the irradiation of sesame seeds .The hydrocarbons, 1,7-hexadecadiene and 8-heptadecene, could be used as markers to identify irradiated sesame seeds. 2-Alkylcyclobutanones were detected only in the irradiated samples at doses >0.5 kGy (2008). Younan Zhu *et al.* had already discussed the initial radicals formed from linoleic acid and linolenic acid irradiated at 77 K and the secondary radicals annealed to room temperature[14]. So it can be supposed that the figure detected by ESR should be contributed from both of linoleic acid and linolenic acid. However, the further qualitative and quantitative analysis is still needed. The mathematical function can used to research on the dose-response curve which can help us to estimate does obtain of unknown samples using re-irradiation in commercial facilities[15,16].

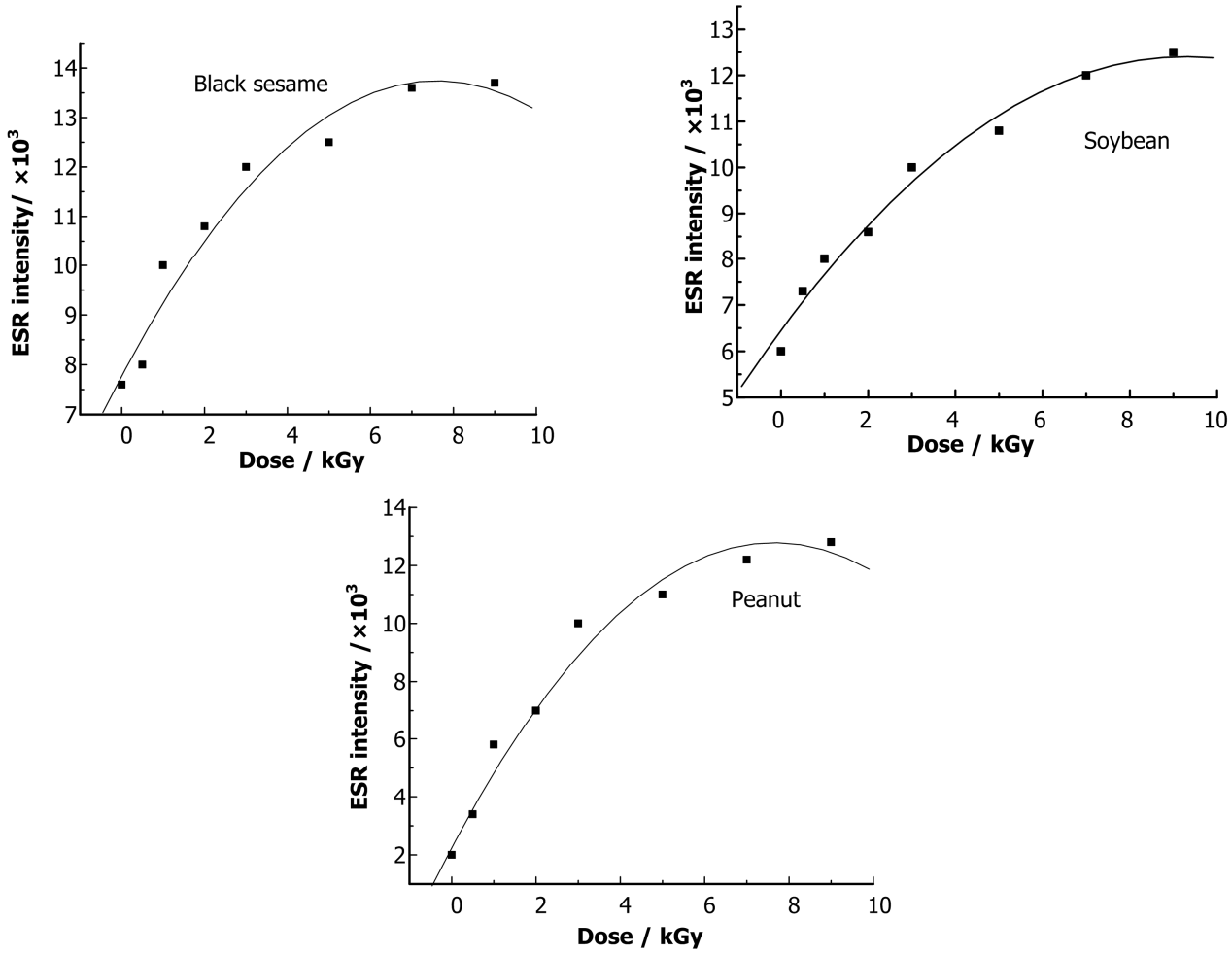

Fig.2 Dose-response curves of the samples exposed to gamma radiation.

Table 1 Fitting function of the samples exposed to gamma radiation.

Samples	Fitting function	R^2
Black sesame	Y =7.82456+1.57885 X–0.10526 X^2	0.9617
peanut	Y =2.45490+2.73454X–0.18103X^2	0.9764
soybean	Y =6.45187+1.28296 X–0.06911X^2	0.9835

3.3 Effection of storage time on the ESR singlet

Oilseed crops samples irradiated at 0, 0.5, 2, 9 kGy were stored at normal laboratory conditions and their ESR spectra were recorded in 6 months with 30days interval. As shown in the Fig 3, with black sesame irradiating at 2 kGy, the signal intensity decreased very fast in the first 30 days and then decreased slowly. After 180 day's storage signal intensity reduced to about 53% of its initial value. Therefore, the distinguishing irradiated and un-irradiated samples can be made even at the end of the storage time of 180 days. On other hand, the fast decrease of signal intensity in the first 30 days may be come from linoleic acid carbon-centered radical who has higher decay constant[17] and similar phenomenon can be seen in the study of chicken meat and pork[18,19]. However, no significant variation with g-factor and line-width were observed in the period of storage time.

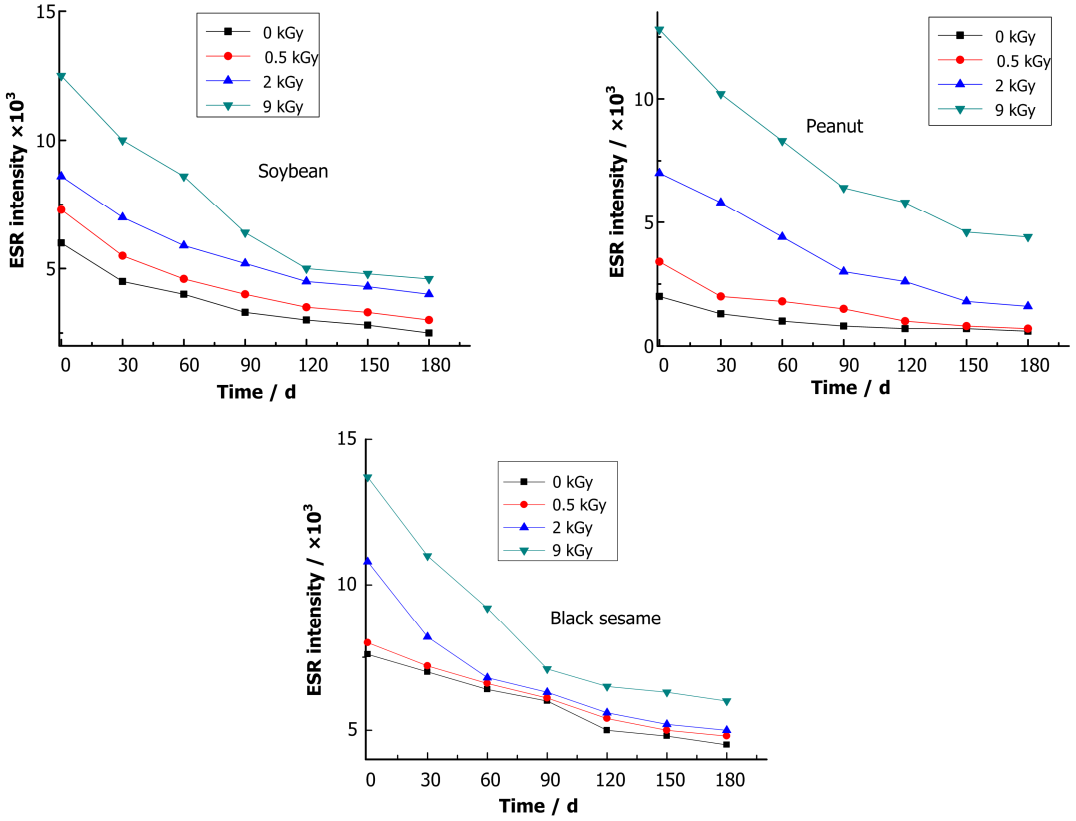

Fig.3 Variation of peak to peak signal intensity with storage time.

4 Conclusion

The intensity of ESR signals of irradiated oilseed samples increase with the absorbed dose. The relationship between signals and absorbed doses can be described by fitting function and the correlation coefficient of the samples were soybean (R^2=0.9835) ≥ peanut(R^2=0.9764) ≥ black sesame(R^2=0.9617). As the ESR singlet of irradiated oilseed samples can be detected in storage time of 6 months, the ESR determination may be used to distinguish weather the oilseeds is irradiated. The forming mechanism with oilseeds suffered from irradiation has been discussed.

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